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Ink-Jet Printing of Cotton with Cationic Reactive Dye Based Inks

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ABSTRACT

The current commercial application of ink-jet reactive inks for cotton fabrics has been through pre-treating with pad liquor prior to printing. In this study, an effort has made to provide a single phase ink-jet printing process for printing cotton fabric using the novel cationic reactive dye in ink's formulation. Cotton fabric was printed with the novel cationic reactive dye and commercial anionic reactive dyes. Color yield and absorbed dye fixations of the printed cotton were analysed at different pH values. The results indicated that printed untreated cotton fabric with cationic reactive dye based ink at optimum pH exhibited higher level of reactive dye fixation than commercial anionic reactive dye based inks on alkali pre-treated cotton fabrics. All reactive dye based inks are demonstrating excellent washing and dry/wet crocking color fastness. The light fastness of each reactive dye based ink fixed to cotton fabrics was moderate. Prog. Color Colorants Coat. 6(2013), 1-8. © Institute for Color Science and Technology.

1. Introduction

Ink-jet printing is a type of non-impact printing with the ability to produce high quality color images. In the last two decades, due to an increasing demand for shorter process runs, faster response times, competitiveness, environmental safety and mass customisation in the textiles industry, the traditional printing techniques have been superseded by digital ink-jet printing technology [1-7]. Cotton and other cellulosic fabrics are commonly printed with commercial reactive dye based inks in the presence of an alkali [8, 9]. The presence of alkali increases the fixation of the dye to the fibers through covalent bond formation via the reaction of the cellulosate anions with the reactive groups of the reactive dye molecules in inks. Unlike the conventional reactive printing on cotton fabric, in which the reactive dyes in the presence of alkali and other chemicals in the form of a print paste are used, in the ink-jet printing process the cotton fabric needs to be pre-treated with alkali prior to printing [10-16]. In the pre-treatment process, the cotton fabric has to be padded with a pre-treatment paste. The pre-treatment paste is usually prepared with either sodium alginate [12-13] or chitosan [14-16] in the

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presence of sodium bicarbonate [17] and urea. Recently, low-temperature plasma (LTP) treatment has been proved to be an effective pre-treatment method for improving the printing process [18]. Following the ink-jet stage, the fabrics are air-dried and put into a steamer to fix the reactive dyes onto the cotton fabric [19]. This is then followed by washing off and drying the fabric. Commercial ink-jet reactive inks are usually based on mono-functional reactive dyes, which have low-to-moderate fixation properties. Consequently, optimising the dye fixation and eliminating the pre-treatment process is very important and highly beneficial from technical, economic and environmental points of view.

The pre-treatment process is energy and time-consuming and the pastes have a short shelf life due to its pH. Using alkali in reactive dye based ink formulation to develop ink-jet printing into a single-phase process by eliminating the necessity to pre-treat fabric is impossible, since the ink will not be stable for more than few hours, as the reactive dye is rapidly hydrolysed, following which it will precipitate within the printing cartridge and block the nozzles of the ink-jet printer.

In previous studies, either the reactive dyes [20] and fabrics were modified [21-23], or fixation-enhancing chemicals were used in the pre-treatment process [12-17, 24] in order to increase the fixation of the reactive ink.

In this study, the aim was to take the first step towards designing and synthesising a new reactive dye for ink-jet printing onto cotton fabric. The idea is about to study the effect of the anionic and cationic groups of the reactive dye molecule. This investigation could reveal a path to a single-phase ink-jet printing technique.

2. Experimental

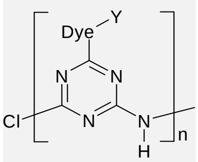
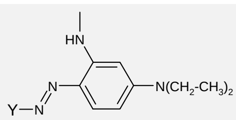
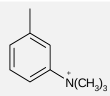
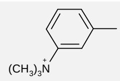
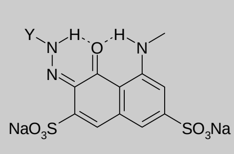
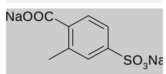
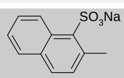
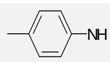
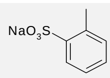
2.1. Materials

The fabric used was 100% singed, desized, scoured and bleached cotton plain weave fabric (98 g/m$^{2)}$ which was supplied from Broojerd Textile Company, Iran. Sodium Alginate was provided by Merck Company, Germany. The commercial anionic reactive dyes (Procion Red PX-8B and Procion Red H-E3B) used for printing cotton was kindly provided by DyStar Company, Germany, Table 1. The novel cationic reactive dye (Table 1) was synthesised according to our previous research [25]. A non-ionic detergent, Synperonic BD 100, Univar, UK, was used in the wash-off process. All other chemicals used in this work were of laboratory grade as received from Merck Company, UK.

2.2. Instrumentation

A laboratory padder, Kimia Behris Company, (Tehran, Iran), was applied for pre-treating fabrics, which then were dried in an Ecocell oven (Munich, Germany). The prepared ink was filtered through 0.45 and 0.2 µm Sartorius Minisart filter (Göttingen, Germany). The fabric was ink-jet printed using a HP DeskJet 5150 printer. A laboratory steamer that was supplied from Kimia Behris Company, (Tehran, Iran), operating at the atmospheric pressure was used for fixation. The dye concentration in the washing baths was determined by absorbance measurements at λ_{max} using UV Ikon 923 Double Beam UV/Visible spectrometer (Saint-Quentin-Yvelines, France).

Table 1: Commercial anionic and novel cationic reactive dyes used for printing the cotton.

Ink	Dye	No. of anionic groups	No. of cationic groups	Main structure	Dye	n	X	Y
1	Dye 1	-	2			1		
2	Procion Red PX-8B	3	-			1		
3	Procion Red H-E3B	6	-			2		

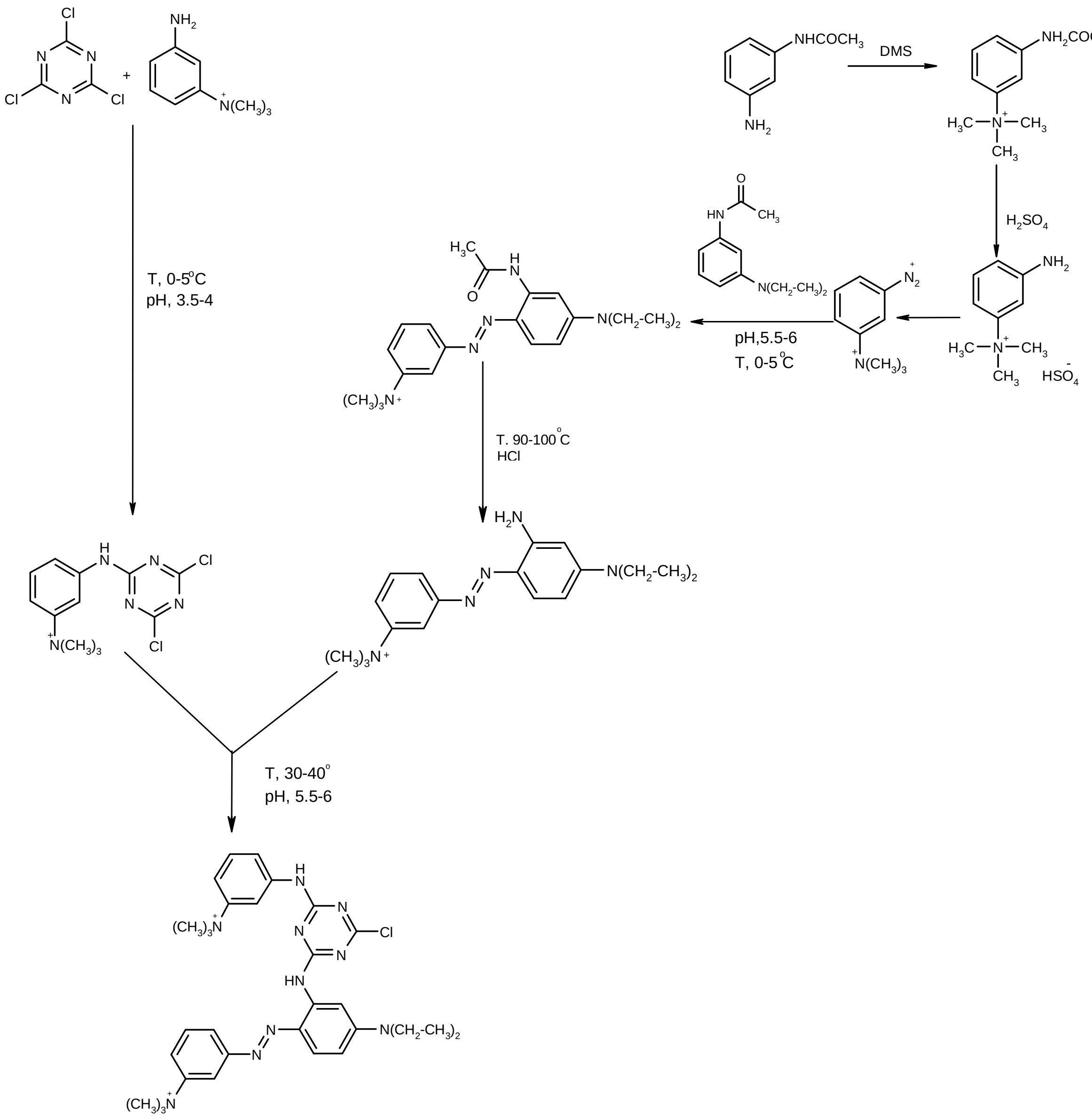
The pH, surface tension and viscosity of inks were characterized using 827 pH meters Metrohm (Herisau/ Switzerland), Tensiometer K100MK2 (Hamburg, Germany) and Brookfield DVII (New Jersey, USA), respectively.

2.3. Preparation of cationic reactive dye (Dye 1)

The Dye 1 was prepared as depicted in Scheme 1 [25].

2.4. Fabric pre-treatment

The pre-treatment paste was prepared using 150 g sodium alginate made from a stock sodium alginate solution, which was made ready by dissolving sodium alginate (50 g) in de-ionised water (0.95 dm^3), sodium bicarbonate (8 g) and urea (10 g). Then the paste was made up to a weight of 200 g with de-ionised water [11-13, 18], which was subsequently mixed thoroughly. The pre-treatment was padded on the cotton fabric using a padding machine with an even pressure of 2.6 kg/m^2 and a constant padding speed of 2.5 r/min until a pick-up of 80% was achieved. The pre-treated fabrics were dried in an oven at 80°C, and then conditioned before ink-jet printing [11-13, 18].



Scheme1: The synthesis of Dye 1.

2.5. Ink-jet printing

The ink-jet printing was carried out on a Hewlett Packard (HP) thermal ink-jet printer (HP DeskJet 5150) at 1200 dpi as a solid square pattern to allow easy color measurement using the ink formulations as illustrated in Table 2. The anionic reactive dyes used in this study were of commercial grade. The novel cationic reactive dye was synthesized as explained above. The ink was made up to 1 dm^3 with de-ionized water. Printing was carried out at four different pH values (5, 6, 7, 8) using McIlvaine buffers, as shown in Table 3 [26]. The prepared ink was filtered through a 0.45 μm filter, and then through 0.2 μm filter to prevent clogging the nozzles before pouring into the cartridge. The viscosity values for the ink-jet inks were between 2 and 2.8 cps which are in the acceptable range for textile ink-jet printing inks [27]. The surface tension values of the formulated inks were in the range of 28-31 mNm^{-1} which are also within the values of typical commercial ink-jet inks for textile printing [28].

After printing, the fabrics were air-dried and then put into a steamer. All the printed fabrics were treated with superheated steam at 110 °C for 10 min for color fixation [11]. The steamed fabric samples were washed with cold water and subsequently washed again in 10 g/dm^3 of non-ionic detergent (Synperonic BD) at 60°C for 10 min until all the un-reacted dye and other chemicals were removed from the fabric's surface [12,13].

2.6. Determination of absorbed dye fixation

To evaluate the fixation percentage of the absorbed dye from the ink-jet printing technique, a methodology was applied from previously established procedures for textile dyeing with the reactive dyes [24, 29-30]. Two equal square pattern printed fabrics of 10 cm ×10cm at 1200 dpi were used to determine the fixation percent; one was printed with the reactive ink on 100% polyester fabric and the other was printed with reactive ink on cotton. The printed polyester fabric with reactive ink was washed off immediately after printing, which was diluted with de-ionised water to 0.5 dm^3 to obtain the total amount of the dye printed on the fabric. The printed cotton fabric with reactive ink was used for steaming and washing to obtain the amount of the washed-off dye after the fixation process, and the wash-off solution was diluted with de-ionised water to 0.5 dm^3. The percentage of the absorbed dye fixation was determined according to equation (1), in which A_0 is the absorbance of the printed dye solution, A_1 is the absorbance of the first wash-off solution, and A_2 is the absorbance of the soaping liquor, which was diluted with de-ionised water to 0.5 dm^3, at the wavelength of the maximum absorption (λ_{max}). Equation (1) is the percentage of absorbed dye fixation.

$$\%F = \frac{A_0 - A_1 - A_2}{A_0} \times 100 \qquad (1)$$

Table 2: Basic printing ink formulation.

Ingredient	g/dm^3
Reactive dye	100
N-methyl morpholine N-oxide	300
2- pyrrolidone	20
Propan-2-ol	25

Table 3: Composition of McIlvaine buffers in a total volume of 100 cm^3.

pH	0.2M Na_2HPO_4 (cm^3)	0.1M citric acid (cm^3)
5	51.50	48.50
6	63.15	36.85
7	82.35	17.65
8	97.25	2.75

2.7. Determination of color fastness properties

Color fastness properties, which are determined by the stability of the dye–fibre system, present an interesting property for quality printing in terms of practicality. For the evaluation of color fastness properties, the color fastness of the ink-jet printed fabrics to light, washing and crocking were determined by AATCC Test Methods 16-2001, AATCC Test Method 61-2001 and AATCC Test Method 8-2001, respectively.

3. Result and discussion

3.1. Effect of pH on printing performance

According to the equilibrium shown in Figure 1, in the presence of water, depending on the pH within the fibre, the cellulose will be ionised to a lesser or greater degree.

The ionisation of cellulose to the cellulosate anion was increased with the pH of the ink, thus the fixation of the dye to the fibers through covalent bond formation via the reaction of the cellulosate anions with the reactive groups was increased over the competitive hydrolysis reaction of the reactive dye. Consequently, pH is a key parameter in influencing the level of fixation of the reactive dye based ink on the cotton fabric. So, it was necessary to determine the best applicable pH for each ink type in order to achieve an optimum dye fixation. A series of prints was evaluated in buffers of different pH values to determine the optimum applicable pH. At pH higher than 8, the reactive dye hydrolysed and might be damaging to the print-head and the cartridge. Therefore, buffers of pH 5, 6, 7 and 8 were made as described in section 2.4 and reactive dye inks were used to print on non-pretreated cotton fabrics. The results depicted in Table 4 indicate an increase in the percentage of absorbed dye with pH. Therefore, the reactive dye based inks, regardless of the type of the used dye, fix more efficiently on cotton fabric at pH 8.

3.2. Effect of cationic groups of reactive dye on the percentage of absorbed ink

Table 4 lists the absorbance of the fixation percentage obtained from the printing of the cotton fabric with cationic reactive dye (Ink 1) and commercial reactive dye based inks (Ink 2 to Ink 3) at optimum pH. From the results shown in Table 4 and Figure 2, it can be seen that the fixation percentage of Ink 1 was higher than that of Inks 2 to 3. The novel cationic reactive dye, which was based on a mono-functional monochlorotriazine reactive group and possessed two cationic groups, exhibited better fixation efficiency, not only when compared to Procion Red PX-8B (Ink 2), which was based on mono-functional monochlorotriazine reactive group and possessed three anionic groups, but also compared to Procion Red H-E3B (Ink 3), which was based on bi-functional monochlorotriazine reactive groups.

At pH 8, the number of cellulosate anion groups increases. These are highly nucleophilic and reactive towards electrophilic reactive groups. Additionally, all the sulphonic acid groups in commercial anionic reactive inks will be de-protonated and anionic, which caused electrostatic repulsion with anionic cellulosate groups.

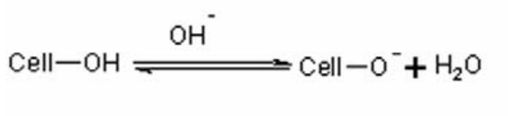


Figure 1: Formation of cellulosate anions.

Table 4: The percentage of absorbed dye after printing the non pre-treated cotton fabric with novel cationic and commercial anionic reactive dye based ink at different pH values.

Ink	pH	5	6	7	8
1(λ_{max}=490)	**%F**	57.15	62.37	68.3	71.6
2(λ_{max}=550)	**%F**	52.09	56.51	61.2	62.09
3(λ_{max}=550)	**%F**	59.87	62.5	65.03	66.01

The cationic group of reactive dye in the ink's formulation contributed to the attraction between the cellulosate anions and the dye. Under these conditions, electrostatic attraction between dye and fibre and the availability of nucleophilic cellulosate anions will be maximised. It was readily demonstrated that high percentages of fixation was attainable with cationic dyes relative to anionic dyes.

The results in Table 5 indicate that, the absorbance of the fixation percentage in the single-phase ink-jet printing process for printing non pre-treated cotton fabric with novel cationic reactive dye based ink was far better than two phase ink-jet printing process for printing pre-treated cotton fabrics with commercial anionic reactive dye based inks.

Therefore, in order to eliminate the pre-treatment process, the single-phase ink-jet printing of cotton fabrics can be realized by using the novel cationic reactive dye based ink as it was formulated.

3.3. Color fastness properties

The results of color fastness to light, washing and crocking of the printed fabrics are given in Table 6.

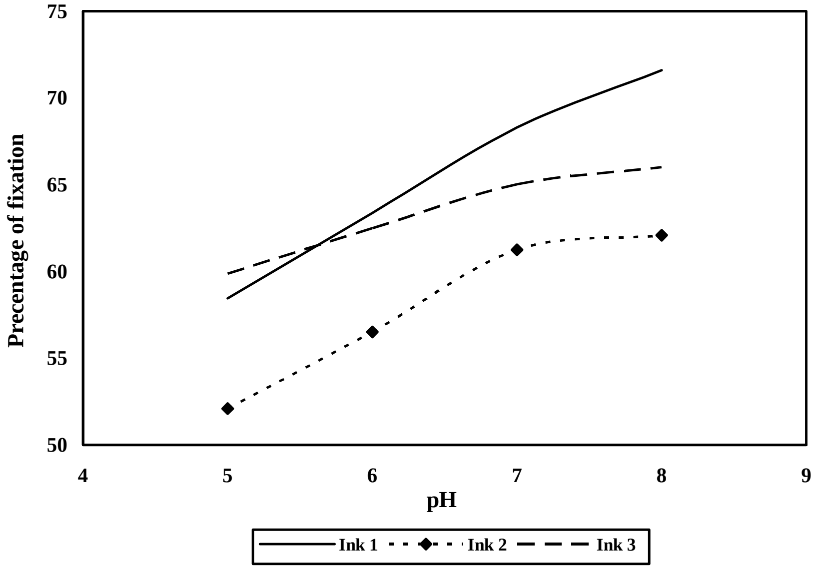


Figure 2: The percentage of absorbed Ink1, Ink2 and Ink3 on cotton fabric at different pH values.

Table 5: the percentage of absorbed dye after printing the pre-treated and non pre-treated cotton fabric with novel and commercial reactive dye based ink at optimum Ph.

Ink		Pre-treated	Non pre-treated
Ink 1	%F	78	71.6
Ink 2	%F	63	62
Ink 3	%F	67	66

Table 6: Color fastness (light, washing, crocking) properties of the printed cotton fabrics

Ink	Light	Washing							Crocking	
		Staining on multi-fibre fabric						Change	Wet	Dry
		Wool	Cotton	Acetate	Nylon	Acrylic	Polyester			
1	3-4	5	5	5	5	5	5	4-5	4	5
2	4	5	5	5	5	5	5	4-5	4	5
3	4	5	5	5	5	5	5	4-5	4	5

The change in the shade and the degree of cross-staining was assessed visually using grey scale. As seen from the results in Table 6, there are no changes in the shade of the printed samples and simultaneously no staining on the adjacent cotton in the case of dry crocking. Very good staining is seen on adjacent cotton in the case of wet crocking. The wash fastness as expected for each ink fixed to cotton fabrics was very good. The light fastness of each printed fabric was moderate.

4. Conclusions

At pH 8 the number of cellulosate anion groups increases, which are highly nucleophilic and reactive towards electrophilic reactive groups. The results demonstrate that at this pH, the cationic groups of the dye based ink contributed to the attraction between the cellulosate anions and the dye. Therefore, under these conditions, electrostatic attraction between dye and fibre as well as the availability of nucleophilic cellulosate anions were maximised. It was readily demonstrated that high percentage of absorbed dye fixation was attainable with cationic dye as compared to anionic dyes. Consequently, the single-phase printing of cotton fabrics can be performed by using the novel cationic reactive dye based ink. The wash and crocking fastness of each reactive dye based ink fixed to cotton fabrics was very good to excellent and the novel cationic dye based ink was not an exception. The light fastness of each reactive dye based ink fixed to cotton fabrics was moderate.

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